This is a Final Report on Contract F49620-96-1-0097, "Studies of Latent Acidity and Neutral Buffered Chloroaluminate Ionic Liquids".

This activity was funded from March 1, 1996 through October 31, 1999 for $452, 623

REPORT DOCUMENTATION PAGE

-AFRL-SR-BL-TR-00-

0263

38

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	31 March 2000	FINAL - 1 March 1996-31 October 1999

4. TITLE AND SUBTITLE

Studies of Latent Acidity and Neutral Buffered Chloroaluminate Ionic Liquids

5. FUNDING NUMBERS

C/F49620-96-1-0097

6. AUTHOR(S)

Robert A. Osteryoung

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

North Carolina StateUniversity
Box 7003
Raleigh, NC 27695-7003

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

AFOSR/NL
801 North Randolph St.,
Room 732
Arlington, VA 22203-1977

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION / AVAILABILITY STATEMENT

APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 Words)*

Studies on ionic liquids composed of aluminum chloride and 1-ethyl-3-methylimidazolium chloride were carried out, with emphasis on understanding and explaining acidity and latent acidity in "neutral buffered" melts. It was found that alkaline earth, as well as alkali metal salts, function as buffering agents, with both showing the "latent acidity" effect. Both Brønsted and Lewis acidities were investigated in an effort to understand the role of the type and concentration of the "buffering" alkali or alkaline earth salt. A silver/silver chloride/chloride ion electrode was found to function as a reversible chloride ion indicator over a very narrow range of melt acidity about the neutral point. This electrode, and relative solubility product measurements, were employed in these studies. It was found that the latent acidity could be explained in terms of the solubility product relationship of the buffering salt, with the salt having the smallest solubility product creating the most acidic melt. Some work was also carried out on non-haloaluminate melts.

14. SUBJECT TERMS	15. NUMBER OF PAGES
Chloroaluminates, ionic liquids, latent acidity, neutral buffered melts	27
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	

SUMMARY OF WORK, 1 March, 1996 – 31 October, 1999

Completed Work

I. Work Carried Out Under Previous Grant

Several manuscripts listed as "in press" or as "submitted" in the Final Report on Contract F49620-94-J-0056, "Chemical Studies in Lewis Acid and Suuperacid Systems", have been published. These include:

J. Fuller, R. T. Carlin, and R. A. Osteryoung, "In-Situ Optical Microscopy Investigations of Lithium and Sodium Film Formation in Buffered Room Temperature Molten Salts", J. Electrochem. Soc.,**143**, L45 (1996).

Richard T. Carlin, Paul C. Trulove, Robert A. Mantz, John J. O'Dea and Robert A. Osteryoung, "Electron Transfer Kinetics for Weakly-Bonded Labile Metal-Ligand Complexes", Royal Society of Chemistry, Faraday Transactions, Special Issue on Electrochemistry Honoring Roger Parsons, **92**, 3969-3973 (1996)

Robert A. Mantz, Paul C. Trulove, Richard T. Carlin, and Robert A. Osteryoung, "Gutmann Acceptor Properties of LiCl, NaCl, and KCl Buffered Ambient-Temperature Chloroaluminate Ionic Liquids", Proceedings of Tenth International Symposium on Molten Salts, R. T. Carlin, S. Deki, M. Matsunaga, D.S. Newman, J. R. Selman and G. R. Stafford, Eds., Proceedings Volume 96-7, pgs. 104-115, The Electrochemical Society, Pennington, NJ (1996).

Dawn King and Robert A. Osteryoung "Acidity of HCl in Neutral Buffered Chloroaluminate Molten Salts", Proceedings of Tenth International Symposium on Molten Salts, R. T. Carlin, S. Deki, M. Matsunaga, D.S. Newman, J. R. Selman and G. R. Stafford, Eds., Proceedings Volume 96-7, pgs. 80-91, The Electrochemical Society, Pennington, NJ (1996)

This prior but now published work was described in the previous Final Report on Contract F49620-94-J-0056.

Most of the work carried out under this present contract has been published, is in press, or has been submitted for publication. Titles and Abstracts of the work follow.

II. Work Completed Under Present Grant

A. Acidity and Latent Acidity in Haloaluminate Ionic Liquids

Acidity of HCl in Neutral Buffered Chloroaluminate Molten Salts, Dawn King, Robert Mantz, and Robert A. Osteryoung, J. Am. Chem. Soc., **118**, 11933-11938 (1996). – (Appendix A- Ref. 141).

Abstract: The Brønsted acidity of HCl in neutral buffered $AlCl_3$-2-ethyl-3-methylimidazolium chloride (EMIC) melts has been compared to the Brønsted acidity of HCl in acidic (55 mol % $AlCl_3$) melts. The acidities were compared using the spectrophotometric indicated method. Arenes were used as the weak indicator bases. The acidity of HCl in the neutral buffered melts was found to be dependent on both the type of buffering agen (LiCl, KCl, and NaCl) and on the concentration fo the metal cation in the melt. An enhancement in Brønsted acidity of HCl is observed in the neutral buffered melts, although to a lesser degree than that in the acidic melts. A Hammett acidity function was determined for a NaCl (originally 55 mol % $AlCl_3$) buffered melt, H_o = -11.3. , H_o = -12.7 for a HCl (1 atm)/LiCl/$AlCl_3$:EMIC (originally 55 mol % $AlCl_3$) buffered melt.

Studies on the Acidity of Neutral Buffered 1-Ethyl-3-Methylimidazolium – $AlCl_3$ Ambient Temperature Molten Salts, Peter Koronaios, Dawn King, and Robert A. Osteryoung, Inorg. Chem. **37**, 2028-32 (1998). (Appendix A – Ref. 147)

Abstract: A series of studies on the acidity of $AlCl_3$-1-ethyl-3-methylimidazolium chloride (EMIC) melts buffered with alkali metal chlorides were carried out. The solubility of HCl, a strong Brønsted acid in these melts, was measured in melts buffered with LiCl, NaCl, and KCl. The solubility of HCl in all three melts is 450 – 475 mM under 1 atm of HCl, approximately the same as that in the acidic ($AlCl_3$ rich) melts. The relative solubility products of LiCl, NaCl, and KCl were measured, and it was found that $K_{sp}(NaCl)/K_{sp}(LiCl) = 72 \pm 6$ and $K_{sp}(KCl)/K_{sp}(NaCl) = 1000 \pm 400$. It is likely that the differences in the acidity of HCl in the various melts are due to the differences in the solubility product of the relevant alkali metal chlorides. These ratios are consistent with the results of previous studies on the acidity of HCl in the melts. The concentrations of the strongly Lewis acidic $Al_2Cl_7^-$ ion in melts buffered with LiCl were measured using an aluminum electrode. The results of the potentiometric work indicate that a melt containing 1 M Li^+ (approximately n_{AlCl_3} / n_{EMIC} R = 1.25:1 prior to buffering) would contain about 200uM $Al_2Cl_7^-$. This corresponds to a solubility product of about $(1.5 \pm 0/5) \times 10^{-12}$ M^2. The liquid junction potentials between unbuffered an buffered melts were found to be about 49 mV x ([Li^+[/M). These results are related to previous work on the acidity of

HCl in these melts, and it is shown that it is possible to explain many of the acidity and latent acidity results on the basis of the solubility products of the alkali metal chlorides.

Gutmann Acceptor Properties of LiCl, NaCl, and KCl Buffered Ambient Temperature Chloroaluminate Ionic Liquids, Robert A. Mantz, Paul C. Trulove, Richard T. Carlin, Terry L. Theim, and Robert A. Osteryoung, Inorg. Chem., **36**, 1227-1232 (1997)

Abstract: Gutmann acceptor numbers have been determined using ^{31}P nuclear magnetic resonance (NMR) for $AlCl_3$/EMIC melts as well as LiCl, NaCl and KCl neutral buffered melts. In $AlCl_3$/EMIC melts, where EMIC is 1-ethyl-3-methylimidazolium choride, the change in Gutmann acceptor number as a function of the $AlCl_3$-EMIC melt ratio is attributed to an equilbirum between a monoadduct of triethylphosphine oxide-$AlCl_3$ and a diadduct of triethylphosphine oxide·$2AlCl_3$. Observed acceptor numbers ofr the neutral buffered melts appears linear with respect to the melt's initial mole ratio of $AlCl_3$:EMIC prior to buffering. The lithium cation appears to be the most Lewis acidic alkali metal cation followed by the sodium and potassium cations. Possible reasons for the change in acceptor number as a function of changing alkali metal cation concentration are presented.

Buffered Chloroaluminate Melts and Latent Acidity, Robert A. Osteryoung, Proceedings of the Twelfth International Symposium on Molten Salts, P.C. Trulove, H. C. De Long, G. R. Stafford, and, Eds., Proceedings Volume, The Electrochemical Society, Pennington, NJ (2000), submitted for publication.

Abstract: Here we discuss the concept of latent acidity in neutral buffered chloroaluminate ionic liquids. Latent acidity involves a reaction between a weak organic base and a Lewis or Brønsted acid in a buffered chloroaluminate melt. The reactions are

$$B: + AlCl_4^- + M^+ = B:AlCl_3 + MCl(s)$$

$$HCl + B: + M^+ \rightarrow B:H^+ + MCl(s)$$

where B: is an organic base that can form an aluminum chloride or protonated adduct, and M^+ is an alkali metal (or alkaline earth) cation. Neither of these reactions will take place in basic or neutral, but unbuffered, melts. Both reactions are driven by the precipitation of the MCl(s), and the acidity depends on the alkali metal cation used, with the acidity increasing $Li^+ > Na^+ > K^+$.

B. Speciation and Buffering Agents

Anodization and Speciation of Magnesium in Chloride-Rich Room-Temperature Ionic Liquids, Joan Fuller, Richard T. Carlin, Peter Koronaios, Robert Mantz, and Robert A. Osteryoung, J. Electrochem. Soc., **145**, 24-28, (1998)

Abstract: Magnesium anodization was examined in room temperature $AlCl_3$:EMIC and $AlCl_3$:DMPIC ionic liquids, where EMIC – 1-ethyl-3-methylimidazolium chloride and DMPIC – 1,2-dimethyl-3-propylimidazolium chloride. For All melts, the $AlCl_3$:organic chloride mole ratio was <1, yielding chloride-rich (i.e., basic) compositions. The rate of magnesium anodizatioin was limited by diffusion of chloride ions to the electrode surface. From the Cottrell slopes for magnesium anodization at a Mg disk electrode, and for chloride oxidation a a Pt disk electrode, the chloride stoichiometry of the anodization process in AlCl3:EMIC was determined to be 4.1 (±0.5), corresponding to the formation of soluble $MgCl_4^{21}$. Similar chloride stoichiometry was found in $AlCl_3$:DMPIC. $MgCl_2$ buffers the melt to approximate neutrality from the basic side, dissolving as $MgCl_4^{2-}$. Magnesium metal was chemically stable in basic $AlCl_3$:DMPIC, but it reacted completely and irreversibly with basic $AlCl_3$:EMIC to produce colored organic byproducts. Some comments are made on the acidity of iCl_2 and $CdCl_2$ in the basic melts.

Alkaline Earth Chlorides as Buffering Agents for Ambient Temperature Chloroaluminate Molten Salts, Peter Koronaios and Robert A. Osteryoung, , Proceedings of Eleventh International Symposium on Molten Salts, P.C. Trulove, H. C. De Long, G. R. Stafford, and S. Deki, Eds., Proceedings Volume 98-11, pgs. 244-251, The Electrochemical Society, Pennington, NJ (1998)

Abstract: We have observed that it is possible to buffer 1-ethyl-3-methylimidazolium chloride (EMIC)-$AlCl_3$ melts to neutrality using $MgCl_2$ or $CaCl_2$. $CaCl_2$ acts as a base buffering acidic ($AlCl_3$ –rich) melts. The electrochemical wondow of both buffered melts is aobut 4.4V, the same as that of a neutral (equimolar) melt and wider than that of an acidic or basic melt. $CalCl_2$ buffers melts by forming the Ca^{2+} ion. $CaCl_2$-buffered melts have greater 'residual' acidity than melts buffered with alkali metal chlorides, as shown by potentiometric analysis with an Ag/AgCl electrode, and studies of the relative solubility products of LiCl and $CaCl_2$.

$MgCl_2$ byffers basic melts by taking up chloride ions to form the $MgCl_4^{2-}$ ion.

Behavior of Oxide Containing Chloroaluminate Molten Salts, Robert Mantz, Jack Summers, and Robert A. Osteryoung, Proceedings of the Eleventh International Symposium on Molten Salts, P.C. Trulove, H. C. De

Long, G. R. Stafford, and S. Deki, Eds., Proceedings Volume 98-11, pgs. 231-243, The Electrochemical Society, Pennington, NJ (1998)

Abstract: The role oxide and hydroxide species play in $AlCl_3$/1-ethyl-3-methylimidazolium chloride (EMIC) melts has been investigated. The oxide and hydroxide species are formed when water is introduced into the melts. Water is an ubiquitous impurity. Melts will be exposed to small amounts of water even when extreme precautions are taken. Both electrochemical and ^{17}O NMR experiments were conducted in order to characterize the effect of oxides and hydroxides on melt properties. The presence of an aluminum hydroxide species causes the melt to behave as a neutral buffered melt. The degree of buffering increases as the hydroxide concentration increases.

$CaCl_2$ and $MgCl_2$ as Buffering Agents for Room-Temperature Chloroaluminate Ionic Liquids, Peter Koronaios and Robert A. Osteryoung, J. Electrochem. Soc., **146**, 2995 -2999 (1999).

Abstract: We have found that it is possible to buffer acidic 1-ethyl-3-methylimidazolium chloride (EMIC)/$AlCl_3$ melts to neutrality using $CaCl_2$ as a buffering agen, while $MgCl_2$ wil partially buffer acidic melts. The buffering reaciont is:

$$MCl_2(S) + 2Al_2Cl_7^- \rightarrow M^{2+} + 4AlCl_4^-$$

Where M is Ca or Mg. From studies using the Ag/AgCl electode as a chloride-sensitive electrode and from measurements of the relative solubility products of LiCl and $CaCl_2$, it appears that the residual concentration of the acidic $Al_2Cl_7^-$ ion in the $CaCl_2$-buffered melts is significantly higher than in any of the other other neutral buffered melts studied so far, making this melt more acidic. Theses melts show the phenomenon known as "latent acidity," forming an $AlCl_3$ complex with the weak Lewis base acetylferrocene. When $MgCl_2$ is used as a buffering agent, the reaction above does not go to completion; it is explained in terms of the solubility product of $MgCl_2$.

Use of the Ag/AgCl/Cl^- Electrode to Estimate Solubility Products in Ambient Temperature Ionic Liquids, Peter Koronaios and Robert A. Osteryoung, J. Electrochem Soc., submitted, December, 1999.

Abstract: The silver-silver chloride electrode has been investigated in 1-ethyl-3-methylimidazolium chloride aluminum chloride room temperature ionic liquids. It was found that the electrode is stable only in a narrow range of acidity around the neutral point, but in this range functions as a reversible Ag/AgCl/Cl^- system. The electrodes were used to make measurements in buffered and neutral buffered melts to estimate the solubility products (and complex formation constants) of several buffering agents; the solubility products are related to the acidity of the buffered neutral melts. In the case of melts buffered with LiCl, NaCl, and KCl,

the values of solubility products obtained were in accord with previous measurements where the ratio of solubility products was determined.

C. Non-Haloaluminate Ionic Liquids

The Room Temperature Ionic Liquid 1-Ethyl-3-Methylimidazolium Tetrafluorborate: Electrochemical Couples and Physical Properties, Joan Fuller, Richard Carlin , and Robert A. Osteryoung J. Electrochem. Soc., **144**, 3881-3886 (1997)

Abstract: The room temperature ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) was demonstrated as a versatile electrolyte by examining three representative electrochemical couples, ferrocene and tetrathiafulvalene oxidations and lithium ion reduction. Square-wave voltammetric data for ferrocene oxidation were fit to a reversible one-electron process using the COOL algorithm to give a half-wave potential of 0.490V vs. Al/Al(III) and a diffusion coefficient of 5.1×10^{-7} cm^2 s^{-1}. The two-electron oxidation of tetrathiafulvalene was reversible and proceeded through two consecutive one-electron steps, although data collected at lower square-wave frequencies indicated a slow precipitation of the TTF species. Lithium ion was reduced to lithium metal at a Pt electrode following the addition of water to the $EMIBF_4$ electrolyte, whereas lithium ion reduction at an Al wire produced the β-LiAl alloy. Conductivities and kinematic viscosities of $EMIBF_r$ were measured from 20 to 100 °C and had values of 14 mS cm^{-1} and 0.275 cm^2 s^{-1}, respectively, at 25°C.

Diffusion Coefficients of Ferrocene in Composite Materials Containing Ambient Temperature Ionic Liquids, Marek Kosmulski, Robert A. Osteryoung, and Malgorzata Ciszkowska, J. Electrochem. Soc., in press.

Abstract: Diffusion coefficients of ferrocene in composite materials composed of the ambient temperature ionic liquids 1,2-dimethyl, 3-(1-propyl) imidazolium tetrafluoroborate (DMPI BF_4) or 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI BF_4) and hexafluoropropylene – vinylidine fluoride copolymer were estimated using chronoamperometry. The values of D obtained with the composite materials based on DMPI BF_4 ranged from 1×10^{-13} to 2.5×10^{-12} $m^2 s^{-1}$ and depended on the composition and pretreatment of the composite material. The latter value is equal to the diffusion coefficient of ferrocene in liquid DMPI BF_4. The values obtained with the composite materials based on EMI BF_4 ranged from 2×10^{-13} to 9×10^{-12} $m^2 s^{-1}$ and they are lower by a factor of more than four than that of ferrocene in liquid EMI BF_4.

III. Personnel

Senior Research Personnel

Dr. Boris Ravdel
Dr. Marek Kosmulski
Dr. Peter Koronaios

Jurnior Research Personnwl

Ms. Dawn King*
Capt. Robert Mantz**

*M.S. received July, 1996
**Not paid on Contract funds; Ph.D. received February 1997.

APPENDIX A

Publications--Grant Related Activity - since AFOSR support initiated.

AFOSR-71-1955; 1 Jan. 1971 - 28 Feb. 1975

1. Janet Osteryoung and R. A. Osteryoung, "The Advantage of Charge Measurements for Determining Kinetic Parameters", Electrochimica Acta, 16, 525 (1971).

2. R. A. Osteryoung, "Introduction to the On-Line Use of Computers in Electrochemistry", Vol. II, "Application of Computers to Chemical Instrumentation", Ed. by Mattson, Mark and MacDonald, Marcel Dekker (1973).

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AFOSR 75-2776; 1 March 1975 - 31 May 1976

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22. Helena Li Chum, D. Koran and R. A. Osteryoung, "Photochemistry of Iron(II)Diimine Complexes in a Room Temperature Molten Salt", J. Am. Chem. Soc., 100, 310 (1978) .

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AFOSR F49620-79-C-0142: 1 June 1979 - 30 Sept. 1980

31. J. Robinson and R. A. Osteryoung, "The Electrochemical Behavior of Aluminum in the Low Temperature Molten Salt System n-Butyl Pyridinium Chloride; Aluminum Chloride and Mixtures of this Molten Salt with Benzene", J. Electrochem. Soc., 127, 122 (1980).

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Appendix B:

Presentations at Meetings Related to Activities on Contract F49620-94-1-0056, 1 January, 1994 - 30 June, 1996

Invited Presentations

1. Robert A. Osteryoung, "Ambient Temperature Chloroalumnate Ionic Liquids: Chemistry, Electrochemistry and Witchcraft". Colloquium, Department of Chemistry, North Carolina State University, Raleigh, NC, October 7, 1996..

2. Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: Chemistry, Electrochemistry and Witchcraft". Colloquium, Department of Chemistry, Colorado State University, Ft. Collins, CO, May 29, 1997.

3. Robert A. Osteryoung, ""Ambient Temperature Chloroalumnate Ionic Liquids: Chemistry, Electrochemistry and Witchcraft". Eltron Research, Inc., Boulder, CO, May 30, 1997.

4. Robert A. Osteryoung, "Some Studies of Latent and Bronsted Acidity in Ambient Temperature Chloroaluminate Molten Salts", Gordon Research Conference on Molten Salts and Metals, Henniker, NH, August, 1997.

5. Robert A. Osteryoung, "Acidity of and In Ambient Temperature Chloroaluminate Ionic Liquids", Frontiers in Electrochemistry Symposium Honoring Stanley Bruckenstein, American Chemical Society Fall Meeting, Las Vegas, Sept. 6-13, 1997.

6. Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: Chemistry, Electrochemistry, and Witchcraft", Department of Chemistry Colloquium, Louisiana State University, Baton Rouge, LA, October 31, 1997.

7. Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: Chemistry, Electrochemistry, and Witchcraft", Department of Chemistry Colloquium, Brooklyn College, CUNY, March 11, 1998.

8. Peter Koronaios and Robert A. Osteryoung, "Alkaline Earth Chlorides as Buffering Agents for Ambient Temperature Chloroaluminate Molten Salts", Eleventh International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, San Diego, May, 1998.

9. Robert Mantz, Jack Summers, and Robert A. Osteryoung, "Behavior of Oxide Containing Chloroaluminate Molten Salts", Eleventh International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, San Diego, May, 1998.

10. Robert A. Osteryoung, "Superacidity in Ambient Temperature Chloroaluminate Ionic Liquids", Symposium on Electrochemistry in Unusual Media and Under Unusual Conditions, The Electrochemical Society, Spring Meeting, San Diego, May, 1998.

11. Robert A. Osteryoung, "Coordination Chemistry, Acid-base Chemistry and Electrochemistry in Ambient Temperature Ionic Liquids", California Institute of Technology, Inorganic Division Seminar, July 29, 1998.

12. Robert A. Osteryoung, "Acidity in Ambient Temperature Chloroaluminate Ionic Liquids", Symposium on Thermodynamic Predictions and Applications", The Metallurgical Minerals and Materials Society of AIME, San Diego, CA, Feb. 28 - March 4, 1999.

13. Robert A. Osteryoung, "Ambient Temerature Chloroaluminate Ionic Liquids – An Overview", International Chemical Conference, Taipei, Taipei, Taiwan, May 13, 1999.

14. Robert A. Osteryoung, "Ambient Temerature Chloroaluminate Ionic Liquids – An Overview", Chemistry Department, National Sun Yat-Sen University, Kaohsiung, Taiwan, May 18, 1999.

15. Robert A. Osteryoung, "Ambient Temerature Chloroaluminate Ionic Liquids – An Overview", Chemistry Department, University of Hong Kong, May 20, 1999.

16. Robert A. Osteryoung, "Buffered Chloroaluminate Melts and Latent Acidity", Twelfth International Symposium on Molten Salts, The Electrochemical Society, Fall Meeting, Honolulu, HI, October, 1999.

17. Paul C. Trulove, Robert A. Mantz, High C. DeLong, and Robert A. Osteryoung, "Studies of Cation Transport in Molten Salts and Molten Salt-Polymer Gels by Pulsed-Field-Gradient Spin-Echo NMR", Twelfth International Symposium on Molten Salts, The Electrochemical Society, Fall Meeting, Honolulu, HI, October, 1999.

Contributed Presentations

1. Boris Ravdel and Robert A. Osteryoung, The Potentiometric and Galvanostatic Behavior of Polypyrrose Films in ambient Temperature Chloroaluminate Molten Salts", North Carolina ACS Section Meeting, Durham, NC, April, 1997.

2. Peter Koronaois and Robert A. Osteryoung, Studies of the Acid-Base Properties of Neutral Buffered Room-Temperature Chloroaluminate Ionic Liquids, North Carolina ACS Section Meeting, Durham, NC, April, 1997.

3. Shawn R. Campagna, Peter Koronaios, Robert A. Osteryoung, and Charles R. Cornman, Spectroscopy and Coordination chemistry in Room-Temperature Ionic Liquids, (Poster), American Chemical Society, Spring Meeting, Anaheim, CA March 21-25, 1999.

4. Peter Koronaios, Robert A. Osteryoung, Acidity of Neutral Buffered 1-ethyl-3-methylimidazoliumChlorideAluminium Chloride Ionic Liquids, North Carolina ACS Section Meeting, Chapel Hill, NC, April 24, 1999